Discriminating Organic Chemical Signatures in Interstitial Waters of Deeply Buried Sediments Using Fluorescence Spectroscopy

Michael S. Twardowski
Department of Research
WET Labs, Inc.
165 Dean Knauss Dr., Narragansett, RI 02882
United States
and
Graduate School of Oceanography
University of Rhode Island
United States
mtwardo@wetlabs2.com

Colleen B. Mouw
Graduate School of Oceanography
University of Rhode Island
United States

Jessica Dombroski
Graduate School of Oceanography
University of Rhode Island
United States

David C. Smith
Graduate School of Oceanography
University of Rhode Island
United States

Excitation-emission matrix (EEM) fluorescence spectroscopy was used to investigate fluorescent dissolved organic matter (FDOM) in interstitial waters of deeply buried sediments cored during the Ocean Drilling Program Leg 201 along the Peru margin. FDOM components that exhibit EEM signatures include aromatic amino acids, polyaromatic hydrocarbons (PAHs), and a group of compounds collectively known as humic substances that are believed to be refractory, diagenetic products of microbial transformations of organic material. Specific component EEM signatures were extracted from the composite EEMs using an eigen-matrix type parallel factor analysis model called PARAFAC, roughly analogous to a principal components decomposition, but in three dimensions. Protein-like and PAH-like EEM components were observed in samples near the surface (<2 meters below seafloor, mbsf). Clear humic-like EEM signatures were observed in every sample analyzed, including Miocene-aged samples from 250 mbsf. Humic-like EEM components matching those found in natural waters and surface sediments were observed throughout the cores, but humic-like components were also identified that have not been observed. Trends in vertical profiles showed an increasingly red-shifted humic-like fluorescence with depth, indicative of a diagenetic process resulting in the humic DOM pool being comprised of successively longer conjugated chain structures over time (i.e., with depth). The ability of fluorescence spectroscopy to discriminate specifically for both labile DOM such as proteins and highly

refractory DOM persisting in extreme conditions over geological timescales suggests that fluorescence spectroscopy is a promising chemical analysis tool for identifying the organic chemical byproducts of possible past and/or present extraterrestrial life.